

REMARKS

The RCE Transmittal for the above-identified application, filed concurrently herewith, is noted. The present amendments and arguments herein, which include claim 37 corresponding to claim 33 refused entry in the Advisory Action mailed March 31, 2003, in the above-identified application, constitute the necessary Submission for the concurrently filed RCE.

That is, the present amendments include amendment of claim 20 to recite that cleaning of the surface of the semiconductor wafer is a cleaning of the surface of the semiconductor wafer covered with the insulating film whose main surface is mainly formed of silicon oxide, consistent with the silicon wafer provided in step (a). See, for example, Embodiment 1 on pages 12-22 of Applicant's specification, particularly the description on pages 14-17 of Applicant's specification.

In addition, in the present Submission, Applicant is adding new claims 34-37 to the application. As indicated previously, claim 37 corresponds to previously submitted claim 33, which was submitted in the Amendment After Final Rejection filed January 23, 2003, this Amendment After Final Rejection being refused entry in the above-identified application as per the Advisory Action mailed March 31, 2003.

Claim 34 recites the same subject matter expressly set forth in claim 26, but is dependent on claim 23; and claims 35 and 36 expressly recite subject matter expressly set forth in claim 37, but are dependent respectively on claims 34 and 23.

As for the subject matter expressly set forth in claims 35-37, note, for example, the first full paragraph on page 6 of Applicant's specification.

Applicant respectfully traverses the rejection of his claims on prior art grounds, as set forth in the Office Action mailed July 29, 2002, and respectfully submits that all of the claims in the above-identified application patentably distinguish over the teachings of the prior art applied in the Office Action mailed July 29, 2002, that is, the teachings of the U.S. Patents to Ohmi, et al., No. 5,990,060 (Ohmi '060), to Wang, No. 6,087,243, to Okutani, No. 5,135,608, to Hazama, et al., No. 5,162,880, to Hwang, No. 5,512,519, and to Ohmi, et al., No. 5,277,835 (Ohmi '835), under the provisions of 35 USC §103.

It is respectfully submitted that these references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, *inter alia*, wherein the surface of a semiconductor wafer, covered with an insulating film whose main surface is mainly formed of silicon oxide, is cleaned using a processing solution which contains hydrogen peroxide, hydracid fluoride salt and water, with concentration of this salt being in a range of about 0.1 - 3 mol/l; and, thereafter, removing the insulating film to expose the surface of the semiconductor wafer; and, after removing the insulating film, subjecting the silicon wafer to a heat treatment to form a gate oxide film over the silicon wafer. See claim 20.

That is, as set forth in claim 20, and as will be discussed further infra, it is respectfully submitted that these references do not disclose, nor would have suggested, wherein the surface of a semiconductor wafer covered with an insulating film whose main surface is mainly formed of silicon oxide is cleaned using the recited processing solution; and, thereafter, there is performed a step of removing the insulating film and thereafter forming a gate oxide film over the silicon wafer. It

is emphasized that according to present claim 20, the step (b) of cleaning is performed using the recited processing solution; and, thereafter, the insulating film is removed; and, thereafter, the step (d) of subjecting the silicon wafer to a heat treatment is performed to form the gate oxide film. Of course, since step (c) follows step (b) and step (d) follows step (c), the step (d) of forming the gate oxide film is performed after the cleaning of the surface of the silicon wafer, covered with the insulating film whose main surface is mainly formed of silicon oxide, using the recited processing solution.

Special problems arise due to the cleaning processing used prior to forming the gate oxide film, when forming the gate oxide film. The present invention, using the recited processing solution at the time, in sequence, of performing step (b), avoids such problems.

In addition, it is respectfully submitted that the references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, inter alia, the other aspects of the present invention as in the remaining, dependent claims, such as (but not limited to) wherein the hydacid fluoride salt is ammonium fluoride or tetraalkyl ammonium fluoride (note claims 21 and 22, respectively); or wherein the processing solution includes HF and HF<sub>2</sub><sup>-</sup> as etching seeds of silicon oxide (note claim 23); or wherein the pH of the processing solution is in a range of 6-11 (note claims 26 and 34); or wherein a step of cleaning during ultrasonic vibration of the processing solution is performed (see claim 25); or temperature of the processing solution during the cleaning as in claim 27; or wherein the insulating film is removed by dipping in a mixed solution of hydrofluoric acid and

water (see claim 28); or the additional drying step, after the insulating film is removed and prior to forming the gate oxide film (note claim 29), with the silicon wafer being immediately transferred to a chamber for forming the gate oxide film, after drying (note claim 30); or the additional heat-treatment in an atmosphere of NO or N<sub>2</sub>O, segregating nitrogen at the interface between the gate oxide film and the silicon wafer (see claims 31 and 32).

Moreover, it is respectfully submitted that the teachings of the applied references neither disclosed nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, having features as discussed previously, and moreover wherein the recited processing solution etches the silicon oxide (which mainly forms the main surface of the insulating film covering the surface of the semiconductor wafer during the cleaning step) but does not etch the silicon wafer. See claims 35-37.

The present invention is directed to a method of manufacturing a semiconductor integrated circuit device, advantageously applied to a cleaning process for a silicon wafer in cleaning the wafer prior to forming a gate oxide film of the device.

In manufacturing a large scale integrated circuit device using a wafer made of mono-crystalline silicon, a so-called RCA wafer cleaning technique has been used, as described in the paragraph bridging pages 1 and 2 of Applicant's specification.

There has been a desire to improve the RCA cleaning technique, and various proposals for improvement thereof have been made, as described on pages 2-4 of Applicant's specification. However, these proposed techniques have been insufficient, particularly in connection with forming an MOSFET which requires a thin

gate oxide film of high quality. See the second full paragraph on page 4 of Applicant's specification. Note also the second full paragraph on page 4, and the paragraph bridging pages 4 and 5, of Applicant's specification, describing problems in connection with these proposed processing techniques. These problems are particularly serious in connection with forming a gate oxide of an MOSFET which requires a thin gate oxide film of high quality.

Against this background, Applicant provides a method having especially advantageous effects for cleaning a semiconductor wafer, in processing prior to forming a gate oxide film of a semiconductor integrated circuit device. Applicant has found that by utilizing a processing solution containing hydrogen peroxide, hydacid fluoride salt and water, the salt being included in an amount of about 0.1 to 3 mol/l, for cleaning the surface of the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide; and with this insulating film thereafter being removed to expose the surface of the silicon wafer; and the silicon wafer then being subjected to a heat treatment to form the gate oxide film, the cleaning can be performed at relatively low temperatures, and the silicon oxide film is cleaned and etched without etching the silicon substrate, so that contamination of the substrate can be avoided. Moreover, through use of the processing solution of the present invention, in processing steps leading up to formation of the gate oxide film, the cleaning can be accomplished in a short time and at a low temperature, without deteriorating flatness of the wafer surface. Note, for example, the first full paragraph on page 6 of Applicant's specification.

Furthermore, through use of the further, oxy-nitrifying processing performed after forming the gate oxide film, nitrogen is segregated at the interface between the

gate oxide film and the wafer, and this segregation of nitrogen at the interface moderates distortion at the interface which induces occurrence of hot carriers, thereby improving reliability of the gate oxide film. See claims 31 and 32. Note the paragraph bridging pages 18 and 19 of Applicant's specification.

Ohmi '060 discloses a cleaning method and a cleaning device which can remove foreign materials deposited on a substrate after removal of photoresist by plasma processing. See column 1, lines 6-10. This patent discloses that foreign materials can be removed under room temperature, by using a cleaning liquid which is a basic and water-soluble fluoride and an oxidizing agent, mixed in pure water. Note column 2, lines 20-29. See also column 2, lines 37-39 and 48-51; column 3, lines 42-47; and column 4, lines 45-50. This patent further discloses that by irradiating ultrasonic waves to the cleaning liquid or pure water, it is possible to improve the cleaning effect. Note the paragraph bridging columns 3 and 4 of this patent. This patent further discloses that the cleaning liquid can be applied not only to removal of photoresist, but also to removal of various types of high polymer organic coating films such as paint or adhesive, films of machine oil, as well as removal of surface surfactant or dye or the like. See column 8, lines 24-34. Note also the paragraph bridging columns 2 and 3; and column 5, lines 7-10, of Ohmi '060. This patent, at the above-referred-to portion of column 8, specifically describes that the technique of Ohmi '060 is advantageously used for removing foreign materials deposited and remaining on the substrate even after a photoresist after ion injection and/or reactive ion etching processing used in a semiconductor production process or in the flat display panel production process.

It is emphasized that Ohmi '060 is concerned with a cleaning liquid and cleaning method removing organic materials, particularly removal of photoresist. It is respectfully submitted that this patent is primarily concerned with removal of photoresist in connection with ion injection or reactive ion etching processes, that is, after formation of the gate oxide and gate electrode. It is respectfully submitted that this patent does not disclose, nor would have suggested, the presently claimed method, including performance of the recited cleaning using the specified processing solution, prior to forming the gate oxide film, and advantages achieved.

Moreover, it is respectfully submitted that this applied reference does not disclose, nor would have suggested, use of the cleaning liquid disclosed in the patent, in processes (including cleaning), leading up to formation of the gate oxide, or concentration of the hydacid fluoride salt in the processing solution as in claim 20.

It is again noted that according to the present invention, the processing solution used can etch the silicon oxide but does not etch the silicon wafer. Note especially claims 35-37. This provides the additional advantage that while cleaning is achieved, a deterioration in flatness of the silicon surface of the silicon wafer can be avoided. Ohmi '060 does not disclose, nor would have suggested, this feature of the present invention, achieved by cleaning utilizing the recited processing solution, at the recited point in the sequence of steps as recited in the present claims.

It is emphasized that according to the present invention, the cleaning technique using the recited processing solution is a cleaning step prior to formation of the gate oxide film. Due to requirements of the gate oxide film, the present invention provides certain advantages, including wherein the surface of the silicon

wafer is not etched. See especially claims 35-37. Therefore, it is possible to remove contamination without deterioration of the flatness of the silicon wafer surface, for example, so that a gate oxide film with a high quality can be advantageously formed according to the present invention.

To the contrary, it is respectfully submitted that Ohmi '060 is concerned with a cleaning step after formation of the gate oxide film. It is respectfully submitted that the cleaning liquid of Ohmi '060 is directed to a cleaning after formation of the gate oxide and after removal of a photoresist mask, and would have neither taught nor would have suggested problems in connection with cleaning prior to forming the gate oxide film, as discussed in the foregoing, and overcoming such problems through use of the processing solution for cleaning as in the present invention.

Thus, it is respectfully submitted, as can be seen in the foregoing, that the purpose and requirements with respect to cleaning prior to formation of the gate oxide film are different from those with respect to cleaning after formation of the gate oxide film; and it is respectfully submitted that Ohmi '060 would have neither taught nor would have suggested the present invention, including cleaning using the recited processing solution as in the present claims, prior to formation of the gate oxide film, and advantages thereof.

The contention by the Examiner in the paragraph beginning on page 4 of the Office Action mailed July 29, 2002, that Ohmi '060 "discloses only process steps (or conditions) necessary to clean a substrate utilizing the processing solution" (emphasis in original), is noted. It is respectfully submitted, however, that Ohmi '060 does not disclose, nor would have suggested, use of the cleaning liquid described therein prior to formation of the gate oxide film. Particularly in light of the unique

problems arising in connection with forming gate oxide films after cleaning, which problems do not arise in cleaning after formation of the gate oxide film (and after formation of the gate electrode), and which problems are overcome by the present invention, as discussed previously, the contention by the Examiner concerning obviousness with respect to Ohmi '060 describing use of a processing solution in a cleaning process, in general, is respectfully traversed.

Moreover, it is respectfully submitted that Ohmi '060 describes use of the disclosed processing solution after formation of the gate oxide film, and would have neither taught nor would have suggested use of the disclosed processing solution in general (that is, at any cleaning step in the semiconductor fabrication process).

It is respectfully submitted that, in the involved art, different cleaning solutions are used prior to, and subsequent to, forming the gate oxide film. In connection therewith, note the enclosed Table 7 on page 254 of the publication Cleaning Technology for Silicon Wafer Surface (February 28, 1995). This shows that different cleaning solutions are used in cleaning prior to and after formation of the gate oxide. It is respectfully submitted that this publication provides further evidence that one of ordinary skill in the art concerned with in Ohmi '060 would not have utilized the cleaning liquid described therein, in a cleaning step prior to formation of the gate oxide film.

It is respectfully submitted that the remaining references as applied by the Examiner in the Office Action mailed July 29, 2002, would not have rectified deficiencies of Ohmi '060, such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Wang discloses a method of manufacturing a semiconductor device including trench isolation. In a description of background art, this patent discloses a trench isolation technique including wherein, after the trench has been formed and filled, heating is utilized to densify the trench fill; and the remaining portion of the pad oxide layer is then removed with dilute hydrofluoric acid, followed by an industrial standard "RCA" clean, with a high quality gate oxide then being grown, followed by polysilicon deposition. Note, column 2, lines 9-41. This patent discloses a method of manufacturing a semiconductor device having an active region isolated by an isolation trench, including formation of a second oxide layer, as described in column 3, lines 32-63. This patent discloses that in accordance with the method described therein, a first sacrificial oxide layer is removed, as by etching with dilute HF followed by a surface cleaning treatment commonly referred to as the "RCA" clean, as with a mixture of hydrogen peroxide and ammonium hydroxide or a mixture of hydrogen peroxide and hydrogen chlorite. A second sacrificial oxide is removed, as by etching employing a dilute HF dip followed by the standard "RCA" clean, exposing a fresh silicon surface, with a thin gate oxide layer being formed on this fresh silicon surface.

Note from column 4, line 66 to column 5, line 28.

Initially, it is noted that according to Wang, the sacrificial oxide layer is removed, and thereafter a surface cleaning treatment is performed. It is respectfully submitted that this disclosure, even in combination with the teachings of Ohmi '060, would have neither taught nor would have suggested, and would in fact have taught away from, a process wherein the cleaning of the surface using the processing solution is performed, and thereafter the insulating film is removed and thereafter the gate oxide film is formed. That is, while Wang initially removes the pad oxide film

and thereafter performs a cleaning, the present invention cleans and thereafter removes the insulating film. Clearly, the teachings of Wang, in combination of the teachings of Ohmi '060, would have taught away from the presently claimed subject matter including wherein cleaning of the surface of the silicon wafer covered with the insulating film whose main surface is mainly formed of silicon oxide is performed using the recited processing solution, removing the insulating film after the cleaning thereby to expose the surface of the silicon wafer; and after such removing, subjecting the silicon wafer to a heat treatment thereby to form a gate oxide film over the silicon wafer, and advantages thereof as discussed in the foregoing.

The contention by the Examiner that both Wang and Applicant are utilizing a common practice, set forth in the last three lines on page 5, and the first four lines on page 6, of the Office Action mailed July 29, 2002, is respectfully traversed. That is, it is emphasized that according to Wang the "RCA" clean is performed after removal of the sacrificial oxide. Such procedure as in Wang would have taught away from the presently claimed process, including wherein the cleaning is performed and thereafter the insulating film is removed (that is, the cleaning is performed prior to removal of the insulating film).

Okutani discloses thin film-forming technology and etching technology in processing wafers used for semiconductor devices. The patent describes a method of producing semiconductor devices including dry and wet processing steps for the wafers, and a step for carrying wafers between the dry and wet processing steps, the dry and wet processing steps and carrying step being continuously carried out in a predetermined atmosphere shutting off the open air. See column 2, lines 26-34. Note also, column 2, lines 42-54; and column 3, lines 57-64.

Even assuming, arguendo, that the teachings of Okutani were properly combinable with the teachings of Ohmi '060 and Wang, such combined teachings would have neither disclosed nor would have suggested the cleaning, subsequent removing and subsequent gate oxide film forming steps in the recited sequence as in the present claims, with the cleaning using the processing solution as recited in the present claims, and the advantages of this process as discussed previously.

Ohmi '835 discloses a surface treatment agent for use in fine surface treatment which is very effective for wet etching of silicon oxide film in the manufacturing process of semiconductor devices, as well as cleaning of fine-treated semiconductor devices. See column 1, lines 12-18. The surface treatment agent includes a mixed solution of fluoric acid, ammonium fluoride and water, the mixed solution containing specified amounts of hydrogen fluoride and ammonium fluoride. See column 3, lines 17-23.

Even assuming, arguendo, that the teachings of Ohmi '835 where properly combinable with the teachings of Ohmi '060 and Wang, as applied by the Examiner, it is respectfully submitted that the combined teachings of these references would have neither taught nor would have suggested the sequence of processing steps, including the cleaning step, insulating film removing step, and gate oxide film forming step, with the cleaning step using the processing solution as in the present claims, and advantages thereof, as discussed previously.

Hazama, et al. discloses a nonvolatile memory cell that is capable of being electrically written, read and erased, and a method of manufacturing this memory cell. A specific example of manufacturing the memory cell is set forth. See, for example, column 4, lines 32ff (note particularly column 4, lines 32-44).

Hwang discloses methods of forming silicon insulating layers in semiconductor devices, in which an oxide layer is formed by regulating the flow of NO and O<sub>2</sub> gas instead of an O<sub>2</sub> gas in a reaction chamber, so that nitrogen may penetrate into a Si and SiO<sub>2</sub> interface in order to improve the reliability of the semiconductor device. Note column 1, lines 6-13.

Even assuming, *arguendo*, that the teachings of Hwang and Hazama, et al. were properly combinable with the teachings of the other references as applied by the Examiner, it is respectfully submitted that such combined teachings would have neither disclosed nor would have suggested the presently claimed invention, including, *inter alia*, the sequencing of processing steps including cleaning the surface of the silicon wafer covered with the insulating film whose main surface is mainly formed of silicon oxide, using the recited processing solution, thereafter removing the insulating film, and, after removing the insulating film, subjecting the silicon wafer to a heat treatment to form a gate oxide film over the silicon wafer, and advantages thereof, as discussed in the foregoing.

In addition, it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested the other aspects of the present invention as in the remaining claims presently in the application, and advantages thereof as discussed previously.

In the paragraph bridging pages 4 and 5 of the Office Action mailed July 29, 2002, the Examiner notes various processing steps described by Wang. However, it must be emphasized that Wang discloses "RCA" cleaning, after removal of the respective sacrificial oxide layers. In the analysis by the Examiner of Wang, the Examiner does not even refer to the sequencing of removal of the sacrificial oxide

layer. It is respectfully submitted that, properly construed, the combined teachings of Wang and of Ohmi '060 would have neither disclosed nor would have suggested the present invention.

Reference by the Examiner to Okutani in connection with claim 26, in the first line on page 7 of the Office Action mailed July 29, 2002, is not understood. It is emphasized that the Examiner has not applied Okutani in connection with claim 26; note the first two lines of Item 2 on page 2 of the Office Action mailed July 29, 2002. See in re Hoch, 166 USPQ 406, 407n.3 (CCPA 1970). Accordingly, it is respectfully submitted that the Examiner cannot presently use the teachings of Okutani in connection with the subject matter of claim 26, as in the Office Action mailed July 29, 2002.

The contention by the Examiner in Item 7 on pages 11 and 12 of the Office Action mailed July 29, 2002, that Ohmi '060 "discloses a critical aspect of the current invention, i.e., Ohmi ['060] discloses a processing solution as currently claimed", is noted. However, it is respectfully submitted that the present claims are directed to a process having recited processing steps, including subjecting the silicon wafer to a heat treatment after removing the insulating film, thereby to form a gate oxide film over the silicon wafer; and wherein prior to removing the insulating film the silicon wafer surface is cleaned using a specified processing solution. Properly construing the presently claimed subject matter as a whole, rather than merely focusing on the processing solution, it is respectfully submitted that the teachings of the applied references would have neither taught nor would have suggested the presently claimed invention.

The contention by the Examiner in the sentence bridging pages 11 and 12 of the Office Action mailed July 29, 2002, is noted. However, it is respectfully submitted that the Examiner has ignored unique problems arising in connection with cleaning prior to formation of the gate oxide film, as discussed previously and as described in Applicant's specification. Properly construed, it is respectfully submitted that, taking the present invention as a whole, the teachings of the applied prior art would have neither disclosed nor would have suggested the presently claimed subject matter.

In view of the foregoing comments and amendments, and also in view of the concurrently filed RCE Transmittal, withdrawal of the finality of the Office Action mailed July 29, 2002 and entry of the present amendments, and reconsideration and allowance of all claims remaining in the application, are respectfully requested.

Attached hereto is a marked-up version of the changes made to the claims by the current Amendment. The changes are shown in the Attachment captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE".

To the extent necessary, Applicant petitions for an extension of time under 37 CFR 1.136. Please charge any shortage in fees due in connection with the filing of

843.37558VX1

this paper, including extension of time fees, to the Deposit Account No. 01-2135  
(Case No. 843.37558VX1) and please credit any excess fees to such Deposit  
Account.

Respectfully submitted,

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"VERSION WITH MARKINGS TO SHOW CHANGES MADE".

20. (Amended) A method of manufacturing a semiconductor integrated circuit device, comprising the steps of:

- (a) providing a silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide;
- (b) cleaning the surface of said silicon wafer covered with said insulating film whose main surface is mainly formed of silicon oxide, using a processing solution which contains hydrogen peroxide, hydacid fluoride salt, and water, concentration of said hydacid fluoride salt in said processing solution being in a range of about 0.1 to 3 mol/l;
- (c) removing said insulating film after said step (b) thereby to expose the surface of said silicon wafer; and
- (d) subjecting said silicon wafer to a heat-treatment after said step (c) thereby to form a gate oxide film over said silicon wafer.